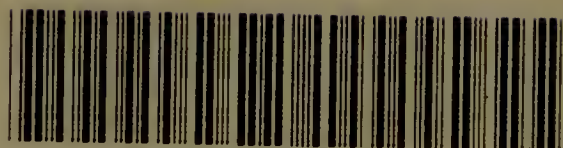


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MISCELLANEOUS  
**CHEMICAL ANALYSES.**

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INAUGURAL DISSERTATION  
PREPARED FOR PROMOTION

TO THE  
**DEGREE**

OF  
DOCTOR OF PHILOSOPHY

AND ADDRESSED

TO THE  
**PHILOSOPHICAL FACULTY**

OF THE  
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## P R E F A C E.

The following analyses were made, during the winter of 1855—6, in the chemical laboratory at Göttingen, under the direction of Prof. Woehler, to whose kindness I am indebted for the substances analysed.

For his valuable suggestions in the different courses of analysis pursued, as well as for his assistance in my chemical studies during the year that it has been my pleasure to enjoy the advantages of his tuition, I take this opportunity to express my most sincere thanks.

The authorities consulted in special cases, are given with their usual abbreviations, in foot notes.

The thermometrical scale of Celsius and the French gramme weights have been used. For the sake of brevity the numbers indicating the different weights of substances used, and obtained, are given as representing *individual quantities*, and the verbs, pronouns etc. are made accordingly, to agree with them in the singular.

The character of the analyses is such as to render it a matter of indifference as to the order in which they are arranged.

They will be found as follows:

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## METEORIC IRON FROM JIQUIPILCO MEXICO.

In no locality, of equal extent, upon the earth's surface, have so many specimens of meteoric iron been found, as on the plateau of Toluca, in Mexico. The fact that large masses of malleable iron occur here was known as early as the latter part of the last century, at which time they were found in such abundance, as to be used for making axes, plough shares and the like.

At a subsequent period, principally through the communications of Chladni <sup>1</sup>, the fact of their occurrence became more generally known in Europe, where the specimens found, in this locality, have been distinguished by different names derived from the particular spot in which each was found. The time at which these masses fell is unknown, but is it highly probable that they all have had their origin in one large meteorite, that was torn asunder in its passage through the atmosphere to the earth, and scattered about as it has been found. The assumption that such a physical phenomenon, as is here indicated

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1) Partsch, die Meteoriten p. 99.

could take place, where the fragments of the mass present no appreciable quantity of elementary constituents, that can be considered as the products of combustion, might well be considered irrational, did not hundreds of observations go to establish its correctness. As examples of such are the cases of the meteoric shower at Aigle. Apr. 1803 <sup>1</sup>, where about 2000 stones, weighing from  $\frac{1}{8}$  of an ounce to 17 $\frac{1}{2}$  lbs. fell to the earth, accompanied with tremendous detonation, like that of heavy artillery. And at a later period, July 1847, at Braunau in Bohemia<sup>2</sup>, where, at break of day, a loud explosion was heard, accompanied with vivid flashes of lightning, at a point supposed to be about 4 miles high, from which two meteoric iron masses descended with great velocity, and struck the earth, at a distance of half a mile from each other.

The most recent information, with respect to the Mexican masses already noticed, is contained in a letter lately received by Prof. Woehler from Hrn. G. A. Stein of Darmstadt.

This latter gentleman was, for many years, a resident in Mexico where he was engaged in mining and smelting. Having heard that a meteoric iron had been discovered in Toluca valley, he, in July 1854

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1) Gehlers physikalisches Wörterbuch B. VI. p. 2089; Pärtisch die Meteoriten p. 16.

2) Jr. Pr. chemie B. XLII, p. 59 u. 828; Jahresbericht Liebig u. Kopp 1847—48 p. 1300.



made a journey to see it. He found it on the Hacienda (plantation) Mani, on the western slope of the mountain range east of Toluca valley. It was a large mass weighing 220 lbs. Hr. Stein succeeded in purchasing it from the owner of the Hacienda; he was informed that the mass was first discovered about 15 years since, on a spot 8 English miles east of Istlohuaca and 2 miles north east of Toluca, in the district of the Indian parish Jiquipilco or Xiquipitco. It lay partly covered with the debris of a small ravine in which a small brook washed its surface. The waters of the brook were, at no time, not even during floods, sufficiently strong to remove the iron mass from its position, which justifies the inference that it fell upon the same spot, in which it was found, which is still further confirmed by the fact that its corners and edges were well defined, and by no means worn away as they would have been had it been rolled down the stream.

Hr. Stein had, on a former occasion, received a mass of meteoric iron from the same man which weighed  $19\frac{1}{2}$  lbs. It had been found on a small hillock in a stony soil near Mani.

It is said that about 20 years ago, a mass of meteoric iron weighing 300 lbs. was found in this region, as also were several smaller pieces. A small piece, weighing 13 lbs. which Hr. Stein obtained, some time since, and which he transmitted to Europe, was doubtless one of the small pieces just noticed above. A specimen of it which was sent to Prof. Woehler, was an-

alysed under his direction by Dr. Uricoechea<sup>1</sup>, of Bogota.

The two large masses, recently found, have also been brought to Europe, by Hrn. Stein. And, at the request of Prof. Woehler, the following analyses were made, to endeavor to ascertain their composition.

For the purposes of analysis, the small chips and filings, made in cutting a piece of about two pounds weight from each of the masses, were used. A few pieces of the instrument, used in cutting them were readily recognized, and removed from the filings and then the latter were separated with a magnet from other foreign substances.

The two pieces cut off, were presented, by Hrn. Stein, to Prof. Woehler, and they are now in his possession, — the following description, of the internal structure of the masses, is drawn from observations and experiments made on these pieces.

## I.

### THE 220 lbs. MASS.

According to Hrn. Stein, this mass was 54 Centimeters long, 34 wide, and 20 thick. The upper surface was more even, and regular than the under, which, in the middle, presented a convex protuberance, in which were several small irregular indentations.

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1) *Annalen der Chemie u. Pharmacie* XCI, p. 249.

The entire surface was oxidised to some depth, and in this oxidised crust, were noticed small particles of sulphide of iron and Schreibersite (phosphor-nickel-iron).

The fracture, in the interior, presents a coarsely lamellar crystalline structure. A smoothly polished surface on being etched with nitric acid, gives very beautiful large and regular Widmannstettian figures the lines of which intersect each other in three predominating directions; they very much resemble those of the meteoric iron of Schwetz. They are characterized by fine lines of a pale yellow metallic substance with much more brilliant lustre, than that of the mass of the iron. These lines, without doubt, consist of plates of Schreibersite, the edges of which are cut by the polished surface.

#### A. ANALYSES OF THE OXIDISED CRUST.

The oxidised crust consisted of small granules with pieces of from 0,5 to 1,0 grms. weight. Ground in a mortar and the mass washed with a rapid stream of water, sharp, irregular, malleable, metallic plates that attracted the magnet, were obtained, showing that the process of oxidation was not complete. Heated in a glass tube, alkaline water was given off, indicating the presence of traces of ammonia.

1. 6,2549 of the oxide lost, on ignition in a platinum crucible, .8174 or 13,06  
4,6186 oxide lost .6226 or 13,48  
mean 13,27.

2. The ignited substance, in coarse granules was heated to dull redness in the bulb of a glass tube and exposed to a dry stream of hydrogen gas as long as moisture was given off. At the end of three hours the bulb was heated as hot as was possible without melting the glass, and when the last trace of oxygen was removed the glass was cooled and weighed: 5,360 ignited oxide lost .9560 or 17,82 p. e.

3. 4,0915 of the reduced oxide (= 4,979 not reduced) was digested with dilute chlorhydric acid at a gentle heat for 12 hours. The hydrogen evolved had the peculiar odor of that obtained with acid and ordinary iron; passed into a solution of acetate of lead a very slight black precipitate was produced, indicating the presence of traces of sulphur. The solution was finally boiled, and filtered from the insoluble residue. Part insoluble in chlorhydric acid.

4. This consisted of (1) porous sandy lumps, many of which retained the original form of the oxide, showing that the silica had penetrated all parts of the crust, (2) brilliant dark gray metallic plates of Schreibersite, (3) dull black irregular granules like coal.

Dried ignited and weighed it gave

.533 insoluble or 10,704 p. e.

ignited oxide.

5. 5,041 of this insoluble residue was treated with aqua regia, and heated for 2 hours. The Schreibersite gradually disappeared leaving the coaly particles untouched with the silica. The solution was evaporated to dryness, to separate silica as usual. It



gave .4602 insoluble silicate and coal which for .533 gives .4866 or 9,948 p. c.

Leaving soluble in aqua regia

.10,704 — 9,948 = 736 Schreibersite .756 p. c.

6. .4571 of the part (§. 5) insoluble in aqua regia was fluxed with three times its weight of a mixture of equal parts of carbonate of soda and potash, and the mass exhausted with water, the solution acidified, evaporated to dryness, to separate silica, as usual; the latter dried ignited and weighed gave .403 which, for the entire residue soluble in aqua regia gives .429 or 8,616 p. c. The coaly granules were still intermixed with the silica; as many as possible of them were selected from the mass for examination. Heated on platina foil, before the blow pipe, no perceptible change was produced, mixed with saltpeter and the crucible heated to redness, they slowly disappeared. The transparent residue, on cooling, was dissolved in water, and a dilute solution of chloride of calcium added. The white precipitate formed was filtered off, and treated with an acid; a brisk effervescence indicated the presence of carbonic acid, formed by the oxidation of the coal (graphite) by the saltpeter.

7. The filtrate (§. 6) from the insoluble silica was boiled, treated with excess of ammonia, and the precipitate of oxide of iron and alumina thrown upon a filter, dried, ignited and weighed, giving .0424 which for the entire insoluble portion (§. 5) gives .0451 or .902 p. c. The principal part of this was oxide of iron, but dissolved in acid, digested with caustic pot-



ash, and ehloride of ammonium added a light precipitate was obtained, which, with proto-nitrate of cobalt, gave the reaction of alumina.

8. The filtrate from the iron and alumina gave, with oxalic acid, evidences of a trace of lime; with phosphate of soda and ammonia a white precipitate of phosphate of ammonia and magnesia, was obtained, which, after being filtered and ignited, gave  $\text{Mg}_2\text{P}$  .0137, (see §. 12).

9. The aqua regia solution (§. 5) was boiled with excess of ammonia and filtered from the oxide of iron precipitated, and the latter fluxed with carbonate of soda and potash, the mass, exhausted with water, filtered from the oxide of iron, the filtrate neutralized with acid, and treated with sulphate of magnesia and ehloride of ammonium, gave the reaction of phosphoric acid, which was further confirmed by molybdate of ammonia.

The filtrate from the preeipitate with sulphide of ammonium gave a black preeipitate, insoluble in dilute chlorhydric acid, which, before the blow pipe, gave the reaction of cobalt free nickel. These are the known<sup>1</sup> reactions of phosphor-nickel-iron.

Part soluble in dilute ehlorhydric acid (§. 3).

10. This was treated with a stream of sulphydric acid for 24 hours. A slight precipitate of sulphur, only, was produced, which being separated, the solution was treated with chlorate of potash, and chlorhydric

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1) Handwörterbuch der Chemie Bd. V, p 222.

acid, boiled to oxidise the iron, carefully neutralized with ammonia and then excess of succinate of ammonia added, and the solution gently warmed for a short time. On cooling, the voluminous red brown precipitate was thrown upon a filter, washed, first with ammonia holding, and then with pure water, dried ignited and weighed, giving 4,6595; of this 3,485 was fluxed with 3 times its weight of a mixture of equal parts of carbonate of soda and potash, the mass exhausted with water, the solution filtered, neutralized with acid and the phosphoric acid thrown down with sulphate of magnesia and ammonia, and weighed as pyrophosphate giving  $\text{Mg}_2 \ddot{\text{P}} .0273$  making for all the oxide of iron .0365 corresponding to  $\ddot{\text{P}} .0231$  or P .0101 or .203 p. c. This leaves oxide of iron 4,6364 which corresponds to 3,2467 or 65,209 p. c. iron.

11. The filtrate from the precipitate with succinate of ammonia (§. 10) was treated with sulphide of ammonium in excess, and filtered from the black sulphides of nickel and cobalt formed. The filtrate, which still contained a small portion of the sulphides, which passed through the filter as such, was slightly acidified with acetic acid and a stream of sulphydric acid passed through it for 6 hours, and after standing 24 hours the clear solution was filtered from the precipitate which, with the first, was dried, removed as much as possible from the filter, the latter burned, and the ash, with the sulphides, boiled with aqua regia, filtered from separated sulphur, and the clear

filtrate boiled with excess of carbonate of soda. The pale green precipitate was thrown upon a filter, well washed, and the oxides while yet moist removed from the filter, and treated with alternate portions of prussic acid and caustic potash and then gently warmed. The oxides dissolved and the solution was boiled to remove excess of cyanhydric acid and convert the cyanide of cobalt and potassium into cobaltcyanide of potassium



The solution was now treated with a stream of chlorine to separate the nickel, as sesquioxide, according to Liebig's latest modification of his method <sup>1</sup>. The black sesquioxide of nickel on ignition weighed .3012 corresponding to .2368 Ni or 4,777 p. c. By an accident the solution containing the cobalt was lost.

12. The filtrate (§. 11) from the oxides of nickel and cobalt, was evaporated to dryness, ignited to expel ammonia salts, and then redissolved in acidified water, and the solution treated with oxalic acid and ammonia, which gave evidence of traces of lime. Treated as in (§. 8) .0193 pyrophosphate of magnesia was obtained, which, added to that of (§. 8), gives  $\text{Mg}_2 \ddot{\text{P}}$  .033 corresponding to .0119 Mg or .241 p. c.

#### CONFIRMATORY ANALYSIS.

13. 2,6162 ignited oxide gave insoluble in chlorhydric acid .294 (after being dried on a filter at 100°)

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1) Ann. der Chemie u. Pharmacie LXXXVII, p. 128.

making 11,23 p. c. In the filtrate nickel and cobalt were separated from iron as in (§. 10). The oxide of iron, weighed, gave 2,4552; deducting phosphoric acid we have  $\text{Fe}_2\text{O}_3$  2,4431 corresponding to 1,7109 Fe or 65,391 p. c.

14. The oxides of nickel and cobalt, were separated from the solution, as in (§. 11) ignited and weighed, giving Ni O and Co O .1612. They were redissolved in acid, reprecipitated by carbonate of soda, redissolved in cyanhydric<sup>1</sup> acid and caustic potash. The redish yellow solution, while yet warm was treated with a triturated mass of peroxide of mercury and boiled till no more oxide was decomposed. The smutty yellowish grey precipitate, with excess of the oxide of mercury, was thrown upon a filter, ignited and weighed, giving Ni O. .146 corresponding to Ni. .115 or 4,395.

Hence

Co O .1612—.146 = .0152 corresponding to Co. .0110 or .456 p. c. Taking the mean of the water determinations, the cobalt of the last, and the first analysis, we have the following summation of results, in which I, is calculated for the reduced substance, II for the dry oxide, and III for the hydrous oxide.

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1) Ann. der Chemie u. Pharmacie LXV, p. 244.



	I	II	III
Water	00,000	00,000	13,27
Oxygen	00,000	17,826	15,447
Iron	79,355	65,209	56,549
Nickel	5,813	4,777	4,127
Cobalt	0,555	0,456	399
Schreibersite	920	756	664
Phosphorus	247	203	177
Alumina and Iron	1,097	902	793
Magnesia	293	241	211
Lime	traces	—	—
Silica	10,485	8,616	7,471
Coal and loss	1,235	1,014	892
	<u>100,000</u>	<u>100,000</u>	<u>100,000</u>

From the last column we can derive the material for the arrangement IV or V below.

	IV		V
(Ni.Co.) O	5,751	(Ni.Co.) O	5,751
Fe <sub>2</sub> O <sub>3</sub>	47,403	Fe O	63,094
Fe	23,363	Fe	6,776
H O	13,270	H O	13,270
Insol. silicates	10,211	Insol.	10,209
	<u>100,000</u>		<u>100,000</u>

It is, however, by no means probable that the distribution of oxygen is right, in either IV or V, as it is certain that peroxide of iron exists in the mass, and it is no less certain that unoxidised iron is also contained therein. It is but rational to assume that iron, in the intermediary stage of oxidation, is also present. Number VI presents such a distribution



as would coincide with this latter view and No. VII is that of an analysis of a bog iron ore from a marshy locality in Nishnei Nowgorod <sup>1)</sup>).

	VI		VII
Fe <sub>2</sub> O <sub>3</sub>	32,750		32,750
H O	13,27		13,000
(NiCo) O	5,751	P O <sub>5</sub>	3,500
Fe O	19,309	Organic Acid	2,500
Fe	18,717	Mn <sub>2</sub> O	1,000
Silicates	10,203	Sand	47,25
	53,98		54,250
	100,00		100,000

A glance at the above numbers will suffice to show the similarity of the constitution of the bog iron ore and the oxide that was formed, from quite different material, in nearly the same circumstances.

The part under brackets, is, with the exception of the nickel and cobalt, in a state of change, in the oxidised crust, and, may be considered foreign to the composition of the mass that would ultimately be formed were the process of oxidation completed. The relation of the water to the peroxide of iron in the crust is, then, about the same as in the bog iron ore. This case is a remarkable one of like agents operating upon unlike materials, and producing, from them similar results. Hermann supposes the bog iron ore to contain a com-

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1) Jr. Pr. Chemie Bd. XXVII, p. 53.

pound  $\ddot{\text{Mn}}\ddot{\text{H}}$  with  $\ddot{\text{Fe}}\ddot{\text{P}} + 6\text{H}\ddot{\text{O}}$  and  $\ddot{\text{Fe}}_3\text{Oks} + 6\text{H}\ddot{\text{O}}$  and that there remains over a compound.

Peroxide of iron	74,83
Water	25,15.

Which gives a relation between the water and peroxide somewhat different from that given for the crust, but it is only intended in these remarks, to point out a general resemblance between the two<sup>2</sup>.

## B. ANALYSIS OF THE INTERIOR.

15. The filings were treated with ether to remove oil that had come from the instrument used in making them, then 6,426 was treated with chlorhydric acid, as in (§. 3) and the gas evolved conducted into a Liebig's potash bulb containing sulphate of copper. The sulphide of copper precipitated gave  $\text{Cu O } .0049$  corresponding to sulphur  $.030$  p. c.

16. The part insoluble in chlorhydric acid, dried at  $100^{\circ}$  on a weighed filter, weighed  $.0578$  or  $.899$  p. c. Under the microscope were observed, (1) brilliant metallic plates of Schreibersite, (2) small black scales of graphite, (3) a few small nearly transparent minerals perhaps olivene, (4) small granules of sand.

17. In nitrochlorhydric acid, the Schreibersite dissolved as in (§. 5) and left insoluble silicates  $.0217$  or  $.3376$  p. c. which consisted of a few granules of graphite with Silica.

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1) Oxycrenic acid.

2) For analyses of similar bog iron ores see Handwörterbuch der Chemie B. VI. p. 808.

18. The nitrochlorhydric acid solution, treated as in (§. 9), gave corresponding results; deducting the p. c. of Silica (§. 17) from that .899 of (§. 16) we get Schreibersite .5614 p. c.

19. The chlorhydric acid solution (§. 15) was treated with sulphydric acid and the slight, yellow precipitate washed on a filter, exhausted with concentrated ammonia and the ammoniacal extract concentrated, oxidised with nitric acid and tested for arsenic by Marsh's method — no arsenic was detected. The part insoluble in ammonia was found to contain copper and tin (see §. 23).

20. The filtrate from (§. 19) was treated as in (§. 10) to separate iron from nickel and cobalt and phosphoric acid. It gave

$\ddot{\text{P}}$  and  $\ddot{\text{Fe}}$  8,3241

$\text{Mg}_2 \ddot{\text{P}}$  .0348 or  $\ddot{\text{P}}$  .0221 or .151 p. c. P.

Hence  $\ddot{\text{Fe}}$  8,302 or Fe 5,8114 or 90,43 p. c.

21. The nickel and cobalt separated as in (§. 11) gave Ni.O .622 corresponding to Ni.4894 or 7,617 p. c. The filtrate from the sesquioxide of nickel was evaporated to dryness, ignited with saltpeter and the residue dissolved in chlorhydric acid, the solution filtered, and the oxide of cobalt thrown down with carbonate of soda, brought upon a filter, washed, dried, ignited and weighed, giving Co.O .059 corresponding to Co. .0464 or .723 p. c.

#### CONFIRMATORY ANALYSIS.

22. 6,704 of the filings gave, after 48 hours digesting, insoluble in dilute chlorhydric .0837 or 1,24 p. c.

23. The ehlorhydrie solution, treated with sulphydrie acid as in (§. 19), gave a yellow precipitate, which was separated, oxidised by nitric acid, the solution evaporated to dryness, ignited and weighed; it gave .0021 or .031 p. c. The weighed residue was treated with dilute nitric acid, filtered from the insoluble portion, and the filtrate concentrated in a test tube, and a drop of ammonia added which gave a blue color. Evaporated to dryness and the residue tested with the salt of phosphorus, and with borax, in the inner flame, it gave unquestionable evidence of copper, and finally, heated with soda on charecoal, the mass ground in an agate mortar, and the coal washed away, metallie scales of copper were obtained. The part on the filter was, with the filter, ignited in a crucible, and the coaly mass mixed with earbonate of soda and heated on coal, and the residue treated as was that of the copper; small scales of tin were obtained.

*In another determination of nickel, cobalt and iron the following results were obtained:*

24. 1,2206 of the small chips of the meteoric iron gave

Fe and P 1,586

also P .015

Hence Fe 1,571 or Fe 1,0997

making 90,09 p. c.

25. The oxides of nickel and cobalt were separated as in (§. 14) giving NiO .1106 or Ni .0866=7,096 p. c. An effort to determine the cobalt by precipi-



tating it as  $(\text{Co}_2 \text{Cy}_6 \text{Cu}_3 + 7\text{H O})$  and then determining the copper in this and from it calculating the cobalt, did not gave a satisfactory result.

The foregoing analyses gave:

	I.	II.
Iron	90,43	90,08
Nickel	7,62	7,10
Cobalt	0,72	—
Schreibersite	0,56	—
Phosphorus	0,15	—
Copper and Tin (oxides)	0,03	—
Sulphur	0,03 insol. in H Cl	1,24
Insoluble Minerals	0,34	
	<hr/> 99,88.	

## II.

### THE 19½ lbs. MASS.

According to Hrn. Stein this mass was 25 centimeters long, 13 wide, and 11 thick, or high. It presented the general form of a large hammer, with an indentation in the middle, as though a smith had attempted to bore a hole through it. Its external surface was much less oxidised than that of the larger mass, which, without doubt, was owing to the difference of the circumstances in which they had lain. Small masses of tombac-colored sulphide of iron, and little plates of Schreibersite, were distributed here and there over the surface. But what renders this meteoric iron particularly interesting, is the



fact that it contains, disseminated through its mass, small clusters of yellowish green granules of olivene. It is most extraordinarily hard, much more so than the large mass, and its fracture is very coarsely lamellarly crystalline. When etched with nitric acid its surface presents very beautiful Widmannstettian figures, very similar to those of the large mass.

#### ANALYSIS.

The largest chips, consisting of pieces of from .1 to .6 grams weight were cleaned with ether as in (§. 15.).

26. 10,3772 was digested, two days, in cold dilute chlorhydric acid. The gas evolved gave no reaction in a solution of sugar of lead, though it possessed the peculiar odor of that obtained with the large mass (§. 3). The part insoluble in cold acid was immediately attacked when the latter was warmed; it constituted a much larger portion than is generally obtained for Schreibersite, much of it however had the appearance of this latter substance; it was separated from the solution.

27. The part insoluble, in cold chlorhydric acid, (§. 26) was digested in boiling concentrated chlorhydric acid, as long as any action took place. The insoluble residue weighed, after being dried at 100°, .0590 which gives 0,568 p. c.

The insoluble residue, to the unassisted eye, presented a black coaly granular mass; under the mi-

croscope, with 60 times linear magnifying power were observed, (1) small metallic plates of a dark steel gray color that attracted the magnet, (2) black granules of graphite not attracted by the magnet, (3) four *ruby-red* translucent granules of sharply defined outlines. Prof. Wöhler found *one* similar granule in a meteoric iron from Rasgati <sup>1)</sup> and Dr. Uricoechea noticed another in an analysis of a meteoric iron from Toluca <sup>2)</sup>, (4) translucent, somewhat rounded granules, probably olivene, (5) transparent granules like sand.

28. The part insoluble in concentrated chlorhydric acid gave, after treating as in (§. 5) insoluble in aqua regia .0105 or .224 p. c.

And soluble in aqua regia  $.568 - .224 = .344$  p. c. The latter treated as in (§. 9) gave the reactions of Schreibersite. The insoluble residue consisted of Silica, with a few black particles of graphite.

29. The part (§. 27) dissolved by concentrated boiling chlorhydric acid, gave no precipitate with sulphydric acid.

The iron was separated from the nickel and cobalt with carbonate of baryta, according to the known method, and the phosphoric acid obtained with the peroxide, determined as in (§. 10) giving

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1) Annalen der Chemie u. Pharmacie Bd. LXXXII. p. 243. Jahresbericht, Liebig u. Kopp 1852, p. 989.

2) Annalen der Chemie u. Pharmacie Bd. XCI, p. 251. Jr. Pr. Chemie Bd. LXIII, p. 317; Jahresbericht Liebig u. Kopp. 1854, p. 917.

$\text{Fe}_2\text{O}_3$  1,009 and  $\text{Mg}_2\ddot{\text{P}}$  .1417 corresponding to  $\ddot{\text{P}}$  .0902 which gives P .0396 or .382 p. c.

30. The filtrate, (§. 29) from the peroxide of iron and excess of carbonate of baryta, was treated with excess of sulphuric acid, filtered from the sulphate of baryta formed, and the oxides of nickel and cobalt precipitated with carbonate of soda. The pale green precipitate, on ignition, gave .1565 which was redissolved in acid, reprecipitated with carbonate of soda, and the freshly precipitated oxides treated with a concentrated solution of oxalic acid, to separate them according to Laugiers method <sup>1</sup>. The excess of oxalic acid was removed from the insoluble oxalates formed, and the latter dissolved in ammonia, and the solution allowed to stand in an open vessel for 3 weeks. Oxalate of nickel separated from the liquid which became colorless, indicating the absence of cobalt. This gives for NiO .1565, Ni .1231 or 1,186 p. c.

31. The cold dilute chlorhydric acid solution (§. 26) gave a slight precipitate with chlorhydric acid, which, treated as in (§. 23), gave unquestionable evidence of the presence of traces of copper and tin.

32. The filtrate from the precipitate by sulphydric acid (§. 31) was boiled with nitric acid, filtered from sulphur, and the clear filtrate divided into 3 equal parts.

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1) Ann. de chemie et de Phys. T. IX, p. 267; Berzelius Jahresbericht Bd. I, p. 53.

33. One of these parts was treated as in (§. 29) to separate iron from nickel and cobalt; it gave  $\ddot{\text{Fe}}$  and  $\ddot{\text{P}}$  4,0301, of which  $\ddot{\text{P}}$  is .0188 (see §. 34) leaving  $\text{Fe}_2\text{O}_3$  4,0113 for one third of the filtrate (§. 32), or  $\text{Fe}_2\text{O}_3$  12,0339 for all of it, which added to the oxide of iron (§. 29) gives, for the entire charge (§. 26)  $\text{Fe}_2\text{O}_3$  13,0429 or Fe 87,984 p. c.

34. Treated as in (§. 10) the oxide of iron found in (§. 33) gave  $\text{Mg}_2\ddot{\text{P}}$  .0295 corresponding to  $\ddot{\text{P}}$  .0188 or P. .00826 which, after multiplying by three, gives .238 p. c.

35. The filtrate from the oxide of iron and carbonate of baryta (§. 33) was treated as in (§. 30) to separate nickel from cobalt. The ammoniacal solution of the oxalates gave, after standing 3 weeks, a pale green precipitate, and the supernatant liquid took on a fine purple color. The precipitate gave on ignition NiO .3115. The filtrate was evaporated to dryness and ignited; the residue, dissolved in acid, precipitated with carbonate of soda, and the precipitate ignited and weighed gave Co. O .0463. The oxides, before separation, weighed .3975. A small loss in the ammoniacal solution of the oxalates made it necessary to calculate the amount of nickel and cobalt present. Thus

$(.3115 + .0463) : .3975 :: (.3115 \text{ or } .0463) : (\text{Ni O or Co O wanted})$ ; which gives NiO .3461 and Co O .0514 which multiplied by 3 give

Ni .817 or 7,87 p. c.

and Co .1213 or 1,07 p. c.



On adding ammonia to the oxalates of nickel and cobalt as above, a very small residue remained undissolved; it was found to contain manganese.

#### CONFIRMATORY ANALYSIS.

36. Another third of the filtrate (§. 32) was used to determine iron nickel, and cobalt.

It gave  $\ddot{\text{Fe}}$ . and  $\ddot{\text{P}}$ . 4,0451, or  $\text{Fe}_2\text{O}_3$ . 4,0263; hence  $4,0263 \times 3 + 1,009 = 13,0879$  or Fe 88,28 p. c. and  $(\text{Ni Co})\text{O}$  .3894, which separated by the proportion of (§. 35) gives Ni 7,71 p. c. and Co 1,04 p. c.

As the foregoing method of separating nickel from cobalt is open to objection the following analysis was made.

37. 2,183 of the filings was digested in aqua regia, and filtered from the insoluble residue which weighed .0269 or 1,236 p. c. Treated as in (§. 29) it gave  $\ddot{\text{Fe}}$  and  $\ddot{\text{P}}$  2,7834;  $\ddot{\text{P}}$  .0426 or P. .0187 or .857 p. c., leaving  $\ddot{\text{Fe}}$  2,7408 or Fe. 1,9185 or 87,88 p. c.

The oxides of nickel and cobalt were separated as in (§. 14). On treating the freshly precipitated oxides with caustic potash and cyanhydric acid, there remained a residue insoluble; it was found to contain manganese, and carbonate of lime, the latter coming from the carbonate of baryta used in separating the iron. This gave

$(\text{Ni Co})\text{O}$ ,  $\text{CaO}$ .  $\text{CO}_2$  and  $\text{Mn}_3\text{O}_4$  .469; of which  $(\text{Ni Co})\text{O} = .2712$  and  $\text{Mn}_3\text{O}_4 = .0061$  or .201 p. c. also NiO .2458 or Ni .1934 or 8,86 p. c.



38. The cobalt was separated, from the filtrate from the nickel, with nitrate of mercury according to Prof. Woehlers modification of Liebig's method <sup>1</sup>.

The cobalticyanide of mercury formed was ignited and the oxide of cobalt weighed: it gave Co O .0248 or Co .0195 or .893 p. c.

39. For a special determination of phosphorus 2,6903 was dissolved in aqua regia, the solution evaporated to dryness, and the residue fluxed with carbonate of soda and potash, as in (§. 10) it gave  $\text{Mg}_2 \ddot{\text{P}}$  .0768 or P. .784 p. c. we then have.

	I.	II.	III.
Iron	87,894	88,280	87,88
{ Nickel	7,870	7,710	8,860
{ Nickel	1,186	1,186	
Phosphorus	.620	.784	.857
Schreibersite	.344	.344	—
Cobalt	1,07	1,040	.893
Insol. Minerals, Graphite	.224	.224	1,236
Manganese	.201	.201	.201
Copper, Tin	traces	—	—
	<u>99,409</u>	<u>99,969</u>	<u>99,927</u>

The above analyses present a much larger p. c. of phosphorus, than is usually found in meteoric iron. The large proportion of it, found in the part insoluble in dilute chlorhydric acid, (§. 26) would indicate that it existed in combination with nickel and iron, as Schreibersite.

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<sup>1</sup>) Annalen der Chemie u. Pharm Bd. LXX, p. 256.

The large p. c. of insoluble minerals in (III.) is due to the fact that filings were used instead of chips, and the insoluble minerals being more brittle, would fall out of the chips amongst the filings in cutting, so that the filings would contain more than a legitimate portion of them.

For the sake of comparison below are given, I. the analysis of the 220 lbs. mass, II. that of the 19 lbs. mass, in which the mean of the iron and phosphorus determination is taken with the 3rd analysis for the other constituents: III. is an analysis by Uricoechea noticed on page 4.

	I.	II.	III.
	Pugh	Pugh	Uricoechea
Iron	90,43	88,018	90,40
Nickel	7,62	8,860	5,02
Phosphorus	0,15	.753	0,16
Schreibersite	0,56	dissolved	2,99
Cobalt	0,72	.893	0,04
Minerals	0,34	1,276	1,11
Manganese	?	.201	traces
Sulphur	.03	.00	traces
Copper and tin	.03	traces	traces
	<hr/> 99,88	<hr/> 100,001	<hr/> 99,72

The *general* similarity of constitution in these three meteorites, is apparent in the above analyses, and yet the difference in the quantity of some of their constituents is such as would seem incompatible with the idea, suggested on page 1, of their common origin, were it not known that different parts of the same

mass have different proportions of elementary constituents and that these differences can well account for the differences of the above analyses.

### III.

#### NATURAL OXIDE OF LEAD.

This mineral was also received by Prof. Woehler from Hrn. Stein.

It is from the mine of San Guillernio district of Zumetohauacan, near Perote in the state of Vera Cruz.

40. *Physical characters.* This mineral presents a finely granular, crystalline structure with brilliant lustrous points over the freshly broken surface, which is of a redish brown color, interspersed with shades of dark steel gray. The external surface has a smutty reddish brown or dark color. Lustre, on the outer surface dull, on the freshly broken surface, submetallic; fracture uneven, irregular and brittle; streak dark brown, tinged with red; hardness, about that of fluorspar; specific gravity, 7,98 in one determination and 7,83 in another.

41. *Chemical characters;* heated in a glass tube, it melts readily to a reddish yellow globule. On charcoal, before the blowpipe, it melts easily and gives a globule of lead with the characteristic incrustation of oxide; fluxed with soda on coal, and the

mass tested for sulphur on a bright silver surface, some trials gave sulphur and others did not, which is due to the presence of small veins of galena that traverse the mass.

#### ANALYSIS.

42. 3,0483 was dissolved in nitric acid, filtered from a small insoluble residue, which on igniting proved to be sulphur, with traces of silica.

The oxide of lead was thrown down as sulphate with addition of alcohol giving  $\text{Pb, S } 3,8492$  or  $\text{Pb } 2,832$  which makes 92,913 p. c.

43. The iron in the filtrate from the sulphate of lead was thrown down as sulphide, the latter re-dissolved and reprecipitated with ammonia as oxide gave  $\text{Fe } .1698$  or 5,57 p. c.

44. 1,5184 treated with nitric acid to determine carbonic acid, in Fritsche's apparatus <sup>1</sup> lost .021 weight making 1,31 p. c.

A second analysis gave for 1,5184 of the mineral  $\text{Pb S } 1,9068$ , or  $\text{Pb } 1,4030$ , or 92,40 p. c.; and  $\text{Fe } .0737$ , or 4,85 p. c. also  $\text{Si } .0023$  or .14 p. c.

	I.	II.
Protoxide of lead	92,91	92,40
Peroxide of iron	5,57	4,85
Carbonic acid	1,38	1,38
Silica	traces	.14
Sulphur and loss	0,14	1,23
	<hr/> 100,00	<hr/> 100,00

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1) Rose analytische chemie Bd. 2, p. 809.



Prof. John <sup>1</sup> analysed a mineral from near the Eschweiler stone coal basins, with essentially the same constitution.

He found Pb 89,16; C 3,84; Ca 0,48; Si 2,40 = 96,88, and sp. gr. = 8,00. The physical characters, as given by him, differ somewhat from those of the present mineral.

Breithaupt <sup>2</sup> notices a mineral supposed to be from Lead Hills Scotland, in which he found 86,62 p. c. lead and 13,38 p. c. oxygen and for which he gives the formula PbO<sub>2</sub>, sp. gr. 9,392 — 9,448.

Dana <sup>3</sup> states, on the authority of Gerolt, that the oxide of lead has been ejected from the volcanoes of Popocatepetl and Iztaccituall in Mexico. But the physical characters of these latter specimens are quite different from that of the mineral just considered.

#### IV.

#### NATIVE LEAD.

The specimen to which the above name is applied is from the same locality as the last. It consisted of a rough irregularly shaped mass, the principal part of which was galena. The native lead was interspersed through it in irregular seams and veins,

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1) Schweiggers Journ. (1812) B. IV, p. 219, also XXXII, p. 106.

2) Jr. Pr. Chemie Bd. X, p. 508.

3) System of mineralogy 1854 vol. II, p. 109; see also Annalen der Chemie und Pharmacie Bd. IV, p. 344.

which on breaking the mass protruded in rough lamina from its fragments. Heated in a glass tube these rough fragments melted down to metallic globules.

## ANALYSIS.

45. 1,3684 of the mass, containing much sulphide of lead, was found to contain 1,1683 lead and .06748 iron which gives

Lead	85,38
Iron	4,93
Sulphur	9,69
Arsenic	traces

	<u>100,00</u>		which can be arranged as
Pb S	55,95	} or {	Pb S    72,42
Pb	36,31		Pb      22,63
Fe S	7,74		Fe       4,93
	<u>100,00</u>		<u>100,00</u>

A mass weighing 83,146 weighed 73,015 in water at 15° which gives

$$\text{sp. gr. } \frac{83,146}{83,146 - 73,015} = 8,2 \text{ nearly.}$$

If we reckon the sp. gr. of lead = 11,4 and that of the sulphide of lead 7,5 it will lead to no material error to consider the specific gravity of the small quantity of iron present as identical with the sulphide of lead. Then we have

$$\frac{82-75}{114-82} = \frac{7}{32} = \frac{\text{Pb}}{\text{Pb S} + \text{Fe}} \quad \text{or nearly 18 p. c.}$$

native lead in the mass.

Unfortunately it is not possible to give here the geological position in which this mineral was found, but it is probable that the native lead resulted from the reduction of galena, in contact with igneous rocks, in the melted state, in the presence of organic matter, as coal, graphite etc.

Other localities noticed are Madeira island, in lava; carboniferous limestone, near Bristol; Kenmare Ireland; gold sand in Ural mountains etc.<sup>1</sup>.

## V.

### SLAG FROM A SILVER FURNACE.

This slag is also from Hrn. Stein; it was obtained from one of his silver furnaces in Mexico, and on account of the technological importance of a knowledge of its constituents, he was desirous to have it analysed. As he did not give the details of the process, by which he obtained it, it is only possible here to say that "it was obtained by melting the oxidised scum, taken from the silver holding galena, the first time it was melted, with (?) slag, in a reverberatory furnace — the Arcos, near Toluca, Mexico".

*Physical characters.* Freshly broken, the surface is steel gray with metallic lustre, soon becoming dull on exposure to the air, indistinctly crystalline interspersed with small round holes giving it a vesicular

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i) See Naumann's *Elemente der Mineralogie*, vierte Aufl. (1855) p. 419; also Dana's *Mineralogy* vol. II, p. 17.

appearance under a lense; hardness 3 to 4; sp. gr. about that of galena.

# ANALYSIS.

46. 1,5821 was treated with nitric acid and boiled, traces of silica remained insoluble. The lead was determined as sulphate

Pb  $\ddot{S}$  .6475 corresponding to Pb .4423 or 27,95 p. c.

47. The copper, antimony and arsenic were thrown down as sulphides, in the acid filtrate from the sulphate of lead.

48. The sulphides of antimony and arsenic were separated with sulphide of ammonium from the sulphide of copper, and then thrown down, in the filtrate from sulphide of copper, with an acid, and the sulphides oxidised with chlorate of potash, and chlorhydric acid, and then, the arsenic thrown down as arsenate of magnesia and ammonia, in the presence of salammoniac and tartaric acid.

The precipitate was dried at 100°, on a weighed filter, giving

(N  $\dot{H}_4$  + Mg $\ddot{2}$ )  $\ddot{A}s$  + H O, .0724, or As. .02847, which makes 1,79 p. e.

49. The antimony, in the filtrate, from the arsenate of ammonia and magnesia, was thrown down as sulphide, and weighed, with excess of sulphur, on a dried filter; the sulphur was oxidised and determined as sulphate of baryta, giving

Sb. and S. .051; Ba,  $\ddot{S}$  .267 or S. .0367.

Hence Sb .0143 or .89 p. c.



50. The sulphide of copper (§. 47) was dissolved in aqua regia, and thrown down with caustic potash, as black oxide giving

$\text{CuO}$  .9981, or  $\text{Cu}$  .7967 or 50,36 p. c.

51. The filtrate from the precipitate with sulphydric acid, (§. 46) was treated with ammonia and sulphide of ammonium, to separate the iron. The sulphide of iron, treated as in, (§. 43) gave  $\text{Fe}_2\text{O}_3$  .0683, or,  $\text{Fe}$  .04781 being 3,02 p. c.

This oxide of iron treated as in (§. 7) gave evidences of the presence of traces of alumina.

52. The filtrate from sulphide of iron, (§. 50) gave a precipitate with oxalate of ammonia, which, on ignition, gave  $\text{Ca}$ ,  $\text{C}$  .0218 corresponding to  $\text{CaO}$  .0123 or 0,71 p. c.

And the filtrate gave, with phosphate of soda, evidences of the presence of traces of magnesia.

53. To determine sulphur 2,2142 was fluxed with three times its weight of a mixture of equal parts of chlorate of potash and carbonate of soda. On cooling, the mass was exhausted with water and the sulphuric acid determined as sulphate of baryta;  $\text{BaS}$  2,427 corresponding to  $\text{S}$  .33421 or 15,09 p. c.

54. A large portion of the slag dissolved in nitric acid, and the concentrated solution treated with chlorhydric acid, gave the reaction of traces of silver.

To sum up we have

	I.		II.
Copper	50,36	$\text{Cu}_2\text{S}$	63,09
Lead	27,95	$\text{Pb}_2\text{S}$	30,10
Iron	13,02	Fe	5,81
Sulphur	15,09	As	
Arsenic	1,79	Sb	
Antimony	.89	S	
Lime	.71	$\text{CaO}$	.71
Magnesia Silica	traces		
Alumina, Silver			
	100,01		99,71

This analysis gives very nearly the formula  $(\text{Pb}_2, \text{Cu}_2, \text{Fe}) \text{S}$ , and the investigations of Bredberg<sup>1</sup> on the artificial production of the metallic sulphides, show that the subsulphides of copper, and lead, and the sulphide of iron might be looked for in a slag obtained by fluxing materials containing these metals with excess of sulphur.

## VI.

### TETRAHEDRITE OR FAHLERTZ.

The specimen examined was from the Guadalupe silver mine, Espiritu santo, near Heutanio, state of Guerrero. Mexico. It was sent to Prof. Wöhler, by Hrn. Stein, accompanied with the statement that he worked the ore for its silver, at one of his smelting

1) Ann. Chem. et Phys. T. XXII. p. 240; Berzelius Jahresbericht Bd. IX. p. 134; Jr. Tech. u. ökonomische Chemie Bd. XII. p. 306.

furnaces in Mexico, and for some reason, not clear to him, it was unusually difficult to get all the silver out of it, and on this account, he was desirous to have it analysed.

*Physical characters.* The specimen was very impure, containing veins of quartz and specks of sulphide of copper, color dark gray, lustre metallic, hardness 4, specific gravity 3.81, streak dark brown.

#### ANALYSIS.

The general course pursued in its analysis is identical with that which H. Rose<sup>1</sup> followed in the analysis of similar substances.

55. The powdered mineral was decomposed, at a dull red heat, in a stream of dry chlorine, and the non-volatile residue treated with nitric acid; the part insoluble in nitric acid became blue on ignition. It was fluxed in a silver crucible with carbonated alkali, the mass exhausted with water, and found to contain silica, alumina, silver and traces of cobalt: 1,310 so treated, gave insoluble in nitric acid .1899 of which .1551 or 11,84 p. c. was silica and silicates foreign to the composition of the mineral.

56. The solution in nitric acid was treated as in (§§. 47. 50) to determine the copper. It gave CuO .418 or .3336 Cu which added to that of the sulphide (§. 57) gives Cu .3943 or 30,10 p. c.

For iron and zinc see (§. 62).

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1) Poggendorff's Ann. d. Chem. u. Phys. Bd. XV, p. 452.



57. The volatile chlorides were all brought into a solution, containing chlorhydric, and tartaric acids, and then the solution treated with sulphhydric acid; the precipitate was, after being separated from the supernatant liquid, digested in sulphide of ammonium, and the black insoluble residue brought upon a weighed filter, dried and weighed, giving sulphide of copper .0915 or copper .0607. Not a trace of mercury could be detected in this residue.

58. The sulphides of antimony and arsenic in the sulphide of ammonium solution (§. 57) were separated and determined as in (§§. 48. 49) giving  $2\text{Mg O}, \text{NH}_4 \text{O} + \text{As O}_5 + \text{H O}$  .038 corresponding to As. .0149 or 1,14 p. c.

$\text{Sb S}_3$  and S .8019;  $\text{Ba O. SO}_3$  3,402 or S .4697, leaving Sb. .3322 or 25,36 p. c.

59. 1,1732 of the mineral was digested in concentrated nitric acid, chlorhydric acid was added to bring the antimony into solution, and separate the silver.

60. Copper, arsenic and antimony were separated from the solution (§. 59) by sulphhydric acid, the precipitate digested in sulphide of ammonium and the insoluble residue dissolved in aqua regia, and the solution tested with sulphuric acid and alcohol for lead; a very slight precipitate was obtained which, before the blow pipe on coal, gave unsatisfactory evidence of the presence of traces of lead.

61. The filtrate from the sulphides of copper etc. (§. 60) was treated with chloride of barium to de-



termine sulphuric acid; it gave  $\text{Ba O. S O}_5$  1,7452; or S .2404 or 20,48 p. c.

62. The filtrate from the sulphate of baryta was treated with carbonate of baryta to separate iron from zinc both of which, when determined, gave  $\text{Fe}_2\text{O}_3$  .0537 or Fe 3,19 p. c.  $\text{Zn O}$  .0872 or Zn 5,97 p. c. The zinc contained a small quantity of cobalt, by which it was rendered blue on heating.

63. The part (§. 59), insoluble in aqua regia, was ignited with resin by which the silver was reduced; the latter was dissolved in nitric acid, filtered and determined as chloride.  $\text{Ag Cl}$  .0334 corresponding to Ag .02513 or 2,14 p. c.

#### CONFIRMATORY ANALYSIS.

64. 1,5383 gave .245 insoluble in aqua regia, of which .0405 was chloride of silver, deducting which we have .2045 or 13,29 p. c. insoluble silicates. The silver was separated as metallic silver, by fluxing with carbonate of soda and exhausting the mass with water and with chlorhydric acid; the metallic globules weighed .0303 making 1,98 p. c.

65. In the filtrate from the insoluble silicates, the copper, zinc and iron were determined as in (§. 56 and 62), giving  $\text{Cu O}$  .551 or Cu .4398 or 28,61 p. c.;  $\text{Fe}_2\text{O}_3$  .081 or Fe .0567 making Fe 3,68 p. c.; and cobalt-holding oxide of Zinc .0987. The latter, heated to redness in a stream of sulphydric acid, and the sulphides treated with acidified water to dissolve the

sulphide of zinc, gave, after igniting the insoluble sulphide of cobalt.

Co O .0094 or Co .0074 or .48 p. c. leaving ZnO .0893 or Zn. 0717 or 4,65 p. c.

66. The filtrate (§. 65), from the part insoluble in sulphide of ammonium gave, with chloride of barium, after separation of the sulphides with chlorhydric acid, Ba O, S O<sub>3</sub> 2,2614 or S 20,26 p. c. The precipitated sulphides after oxidation gave 2Mg O. As O<sub>5</sub> .027 or As .013 or .84 p. c. The solution containing the antimony was lost; it is determined from the loss in II. below

	I.	II.
Copper	30,10	28,61
Silver	2,14	1,98
Iron	3,19	3,68
Zinc	} 5,97	4,65
Cobalt		0,48
Lead	?	?
Antimony	25,36	(26,21; loss)
Arsenic	1,14	0,84
Sulphur	20,48	20,26
Silicates	11,84	13,29
	<hr/> 100,12	<hr/> 100,00

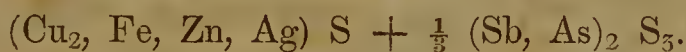
As the silicates and cobalt are foreign to the constitution of Fahlerz, they must be thrown out of the analysis before we compare it with that of other minerals of the same species.

Below, I and II are the reduced columns, and III

is a mean of these two; IV is the relative number of atoms of each substance present:

	I.	II.	III.	IV.	
Copper	34,06	33,18	33,62	.531	Cu <sub>2</sub>
Silver	2,43	2,29	2,36	.021	Ag
Iron	3,61	4,27	3,94	.140	Fe
Zinc	6,76	5,39	6,07	.180	Zn
Antimony	28,67	30,40	29,54	.230	Sb
Arsenic	1,30	.98	1,14	.014	As
Sulphur	23,17	23,49	23,33	1,459	S
	100,00	100,00	100,00		

This corresponds very nearly to the formula



Prof. Rose<sup>1</sup> gives the analysis of a Fahlerz from Clausthal with nearly identical pr. ct. of constituents.

Berthier<sup>2</sup> gives several methods of obtaining silver from its ores; the following of which were tried

1st. 14,8166 of the mineral fluxed with 17 of litharge and 5 of salpeter, gave a metallic mass weighing 13,209 which dissolved in nitric acid and the silver determined as chloride in this solution, gave 1,89 p. c.

2nd. 9,471 fluxed with 28 acetate of lead and 19 of potash, gave a metallic mass, and this treated as above gave 1,53 p. c. silver.

3nd. 9,648 fluxed with 4 times its weight of saltpeter gave no reduced metal.

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1) Poggendorff's Annalen Bd. XV, p. 576.

2) Traité des essais par la voie sèche T. II, p. 826.

It is highly probable that the difficulty, of which Hr. Stein speaks in obtaining the metal from the ore is due to the presenee of the silica, and it might be obviated by the use of an alkaline flux.

## VII.

### PHOSPHATE OF TIN.

Reynoso <sup>1</sup> has given a method for the determination of phosphoric acid, which is dependent upon the faet, first notieed by him, that this aeid, when boiled with nitric acid, in the presenee of tin, forms a eompound with the peroxide of tin produceed, which is insoluble in nitric acid, while nearly all other substances, in the same eircumstanees, are soluble and, therefore, can be removed.

As a method so simple for determining phosphoric acid, is of great importance in the analysis of soils, ashes of plants, etc., at the suggestion of Prof. Woehler, the following experiments were made, to aseertain the aeouraey of the same, and also the character of the insoluble eompound formed, on which its value, for quantitative purposes, is dependent

*First experiment*, — to see if the phosphoric aeid all remains behind insoluble when excess of tin is present.

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1) Compt. rend. XXXIII, p. 385; Jr. Pr. chemie Bd. LIV, p. 261; Annal. der Chemie u. Pharmacie Bd. LXXX, p. 354; Liebig u. Kopp Jahresbericht (1851) p. 613.



67. The phosphoric acid of osteolite, a white amorphous pulverable chalk-like mineral, was first determined. In this mineral Bromies, Reutz, and Ewald<sup>1</sup> found

PO <sub>5</sub>	36,88;	37,41;	37,16
SiO <sub>3</sub>	4,50;	2,75;	2,03

The powdered mineral was dried at 120° and

68. 1,4845 boiled with nitric acid; it gave insoluble silicates .0713, or 4,80 p. c.

The filtrate was evaporated nearly to dryness, and then 2,5 of tin foil and excess of strong fuming nitric acid added, and after the intense action had subsided, the solution boiled till no more red fumes were evolved. The somewhat concentrated solution was treated anew with acid, and boiled for some minutes to insure complete oxidation, to peroxide of tin. After driving off a part of the excess of acid, boiling water was added, and, after boiling a few minutes, the insoluble portion was separated, on a filter, from the solution; dried, ignited and weighed it gave PO<sub>5</sub> and Sn O<sub>2</sub> 3,728, of which the Sn O<sub>2</sub> was 3,180 leaving PO<sub>5</sub> .548 or 36,91 p. c.

69. 1,197 was treated as above, except that the silica was not separated, and on addition of boiling water, to the oxidised mass, it was filtered without further boiling; it gave PO<sub>5</sub>, Sn O<sub>2</sub> and Si O<sub>3</sub> 3,047, of which Sn O<sub>2</sub> was 2,544, (2. of Sn having been

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1) Annal. der Chemie u. Pharmacie Bd. LXXIX, p. 1; Liebig u. Kopp Jahresbericht (1851) p. 813.

used) leaving .503, or 42,02 p. c.,  $\text{P O}_5$  and  $\text{Si O}_3$ ; deducting the  $\text{Si O}_3$  of (§. 68) we get  $\text{P O}_5$  37,22 p. c.

70. 1,2626, oxidised with 2. of tin, then treated with *cold* water and filtered cold, gave  $\text{P O}_5$ ,  $\text{Sn O}_2$  and  $\text{Si O}_3$  3,0702,  $\text{Sn O}_2$  2,5440, leaving  $\text{P O}_5$  and  $\text{Si O}_3$  41,67 p. c. or  $\text{P O}_5$  36,87 p. c.

71. *With phosphate of soda:* 1,143 ignited phosphate of soda was dissolved in water, 2,1445 tin added, and the whole boiled with nitric acid, as in (§. 68). It gave  $\text{P O}_5$  and  $\text{Sn O}_2$  3,3349 of which  $\text{Sn O}_2$  is 2,7299 leaving  $\text{P O}_5$  .6070 or 53,105.

72. .146 ignited phosphate of soda, 6. of a mixture of common alum, and green vitriol, and .3845 tin gave, after treating as in (§. 68), with nitric acid, insoluble .5707, of which .4891 was  $\text{Sn O}_2$ , leaving .0816, or 55,88 p. c. Pyrophosphate of soda contains 53,37 p. c. phosphoric acid; the excess (2,57 p. c.) found above, was in part owing to insoluble silicates in the vitriol and alum used, and in part due to oxide of iron that was not entirely washed out of the insoluble residue.

The foregoing results indicate a satisfactory degree of accuracy for the method; it must however be observed that traces of phosphoric acid could, with molybdate of ammonia, be detected in the concentrated filtrate from the insoluble portion formed, as also could traces of tin be detected in the same with sulphydric acid. The former could not be detected with ammonia and a soluble magnesia salt.

The presence of tin in the filtrate was doubtless owing to traces of chlorhydric acid, that were found in the nitric acid used, together with traces of the same from the chlorides in the osteolite (see H. Rose's analytische Chemie (1851. Auflage) Bd. II, p. 282). In drying and weighing the insoluble compound, too much care cannot be taken to keep it in perfectly dry air, as it absorbs water with great rapidity which would lead to a false result. It has been advised that it should be weighed before it was entirely cold, in order to avoid absorbtion of moisture; but every one, who is accustomed to accurate weighing, will know that weights taken thus, are not reliable.

73. The conditions of success, by this method may be summed up as follows.

1st. Pure tin must be used, or if it be not pure the pr. ct. of impurity, must be known, *providing*, that impurity be not antimony or arsenic, in which case *it is not* adapted to the purpose at all.

2nd. The solution, from which the insoluble peroxide of tin and phosphoric acid, is filtered, must be *free* from chlorhydric acid.

3rd. In oxidising, a pretty free excess of nitric acid must be used, and the solution well boiled, before addition of water. If *cold* water be added, and an attempt be made to boil, it almost invariably thumps, so as to render the process disagreeable if not impracticable. This is avoided by adding boiling water, and filtering either with or without further boiling. If cold water be added after the process



oxidation is complete, and the solution be filtered without heating, it filters very slowly, but is unattended with other inconveniences.

*Second experiments*, — to learn the character of the compound formed by the peroxide of tin and phosphoric acid.

74. 1. of tin was oxidised with nitric acid, in the presence of excess of common phosphate of soda, from which was obtained

$$\begin{array}{rcl} \text{P O}_5 \text{ and Sn O}_2 & 1,6628 \\ \text{of which SnO}_2 \text{ is} & 1,272 \text{ or} \\ & \text{P O}_5 \text{ 23,51} \\ & \text{Sn O}_2 \text{ 76,49} \\ & \hline & 100 \end{array}$$

Two other determinations with common phosphate gave

$$\begin{array}{rcl} \text{P O}_5 & 34,6 & 28,5 \\ \text{Sn O}_2 & 55,4 & 71,5 \\ & \hline & 100 & 100 \end{array}$$

75. 1. of tin with pyrophosphate of soda in excess gave

$$\begin{array}{rcl} \text{P O}_5 \text{ and Sn O}_2 & 1,6962 \text{ or} \\ \text{P O}_5 & 25,01 \\ \text{Sn O}_2 & 74,99 \\ & \hline & 100 \end{array}$$

Another determination with pyrophosphate of soda in excess, gave

$$\begin{array}{rcl} \text{P O}_5 & 27,4 \\ \text{Sn O}_2 & 72,6 \\ & \hline & 100 \end{array}$$



We then have

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
PO <sub>5</sub>	23,51;	25,01;	27,4;	34,6;	28,5;	24,11;	32,4;	51,0
SnO <sub>2</sub>	76,49;	74,99;	72,6;	65,4;	71,5;	75,89;	67,6;	49,0

In the above VI, VII and VIII are respectively the proportion between the PO<sub>5</sub> and SnO<sub>2</sub> in tribasic, bibasic and monobasic phosphate of peroxide of tin.

It would seem that all three of them are formed, in variable proportions, in the process given above, since, while I corresponds very nearly with VI, IV is above VII in its p. c. of phosphoric acid.

*Third experiment* — to ascertain whether or not the peroxide of tin combines in its nascent state only.

76. 1. of tin, treated with nitric acid and boiled to complete oxidation and then phosphate of soda in excess added, and the solution boiled with nitric acid 15 minutes and then filtered, gave

PO <sub>5</sub>	9,0
SnO <sub>2</sub>	91,0
	<hr/> 100

which goes to show that the combination takes place in the nascent state, with by far the greatest facility.

That pyrophosphate of soda should not give pyrophosphate of tin, is to be expected in view of the manner in which it was treated, as the treatment would convert the pyro into common phosphoric acid.

The phosphate of tin, as obtained in the foregoing processes is a scaly, brittle white mass, insoluble in water, and acids and infusible in the flame of a Ber-

zelius alcohol lamp. Fluxed with phosphate of soda or potash it gives phosphate and stannate of alkali.

*Fourth experiment* — to combine phosphoric acid with peroxide of tin in a solution of perchloride of tin.

77. Pyrophosphate of soda added to a solution of perchloride of tin, at first gave no precipitate, but after standing some hours, the solution became milky, and, at the end of two days, the entire fluid became semisolid and presented a gelatinous, translucent mass, having a fine opalescent appearance, with beautiful play of colors. With slight blows upon the glass containing it, a tremulous vibration, accompanied with a slight musical tone, similar to that produced in like manner under certain circumstances with gelatinous silica, was produced.

When common phosphate of soda was added to a solution of perchloride of tin, all the tin was precipitated. The amorphous voluminous white precipitate, after being well washed on a filter, was divided into two parts, one of which was used, while yet moist, to determine the relation between the quantity of tin and phosphoric acid present, and the other to determine the water present, after being dried at 100°.

Two determinations of the tin and phosphoric acid were made.

78. One was made by dissolving the moist precipitate in sulphide of ammonium, and precipitating the sulphide of tin with an acid, filtering, igniting and weighing the oxide formed.

The phosphoric acid was thrown down from the

filtrate from the sulphide of tin, and determined as in (§. 10). This gave

$$\begin{array}{rcl} \text{Mg}_2 \ddot{\text{P}} & .1719 \text{ or } \ddot{\text{P}} & .109 \text{ or } 23,57 \\ \text{Sn O}_2 & .3534 & \text{or } 76,43 \\ & & \hline & & 100,00 \end{array}$$

79. Another analysis was made by dissolving the moist precipitate in chlorhydric acid, and precipitating the tin with sulphydric acid, filtering off the sulphide formed, igniting and weighing and then determining the phosphoric acid as in (§. 78).

This gave  $\text{Mg}_2 \ddot{\text{P}}$  .237 or  $\ddot{\text{P}}$  .15078 and  $\text{Sn O}_2$  .458. giving  $\text{P O}_5$  24,77

$$\text{Sn O}_2 \text{ 75,33}$$

Which corresponds very nearly with tribasic phosphate of peroxide of tin;  $3\text{Sn O}_2 + \text{P O}_5$

	found		calculated
$\text{P O}_5$	23,57	24,77	24,11
$(\text{Sn O}_2)_3$	76,43	75,33	75,89

The other part of the white precipitate was dried at  $100^\circ$  and then ignited. On ignition it lost 13,26 p. c. of its weight at  $100^\circ$ .

This pr. ct. of water corresponds very nearly to 5 equivalents making  $(\ddot{\text{S}}_3 \ddot{\text{P}} + \ddot{\text{H}}_5)$ , but since the body is not crystalline this coincidence may be accidental. The salt dried at  $100^\circ$  becomes very hard and brittle, breaking with conchoidal fracture, presenting translucent edges with the color of opal.

80. It may be remarked in conclusion that to apply the foregoing method, to the purposes of ash, and soil analyses, for which, in many cases, it ap-

pears to be specially adapted, the best plan would be to exhaust the soil with nitric acid, determine chlorine in the acid extract as usual, with nitrate of silver, and then in the concentrated chlorhydric-acid-free filtrate, determine the phosphoric acid as above; by this means, the error due to the presence of chlorhydric acid will be avoided.

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#### ERRATA AND ADDENDA.

P. 1, 6th line for the bottom for "is it" read it is.

P. 2, to reference 2, add, Clark's Inaugural Dissertation (Gottingen 1852) p. 52.

P. 3, 4th line from the top, for Hrn, read Hr.

P. 5, 10th line from the bottom, (also page 16, 13th line from the top) for "Morter", read Mortar.

Also, to the end of each of the three last lines add, p. c.

P. 8, 7th line from the bottom, for, "cobalt free", read cobalt-free.

P. 15, 3rd line from the top, omit "that".

*Remark;* the errors, in punctuation, are not deemed of sufficient importance to have a place here.

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